SRNL-STI-2011-00586
Revision 0

Keywords: *Solvent Extraction, Gas Chromatography – Flame Ionization Detector*

Retention: *Permanent*

Results of Analytical Sample Crosschecks for Next Generation Solvent Extraction Samples: Isopar® L Concentration and pH

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September 2011

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Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

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Printed in the United States of America

Prepared for
U.S. Department of Energy

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EXECUTIVE SUMMARY

As part of the implementation process for the Next Generation Cesium Extraction Solvent (NGCS), SRNL and F/H Lab performed a series of analytical cross-checks to ensure that the components in the NGCS solvent system do not constitute an undue analytical challenge.

For measurement of entrained Isopar® L in aqueous solutions, both labs performed similarly with results more reliable at higher concentrations (near 50 mg/L). Low bias occurred in both labs, as seen previously for comparable blind studies for the baseline solvent system. SRNL recommends consideration to use of Teflon™ caps on all sample containers used for this purpose.

For pH measurements, the labs showed reasonable agreement but considerable positive bias for dilute boric acid solutions. SRNL recommends consideration of using an alternate analytical method for qualification of boric acid concentrations.

LIST OF ABBREVIATIONS

ANL - Argonne National Laboratory
GC-FID – Gas Chromatography with Flame Ionization Detector
ICPES – Inductively Coupled Plasma Emission Spectroscopy
MCU - Modular Caustic-Side Solvent Extraction Unit
NGCS – Next Generation Cesium Extraction Solvent
ORNL - Oak Ridge National Laboratory
SRNL - Savannah River National Laboratory

1.0 Introduction

The Savannah River Site currently utilizes a solvent extraction technology to selectively remove cesium from tank waste at the Modular Caustic-Side Solvent Extraction Unit (MCU). This solvent consists of four components: the extractant – BOBCalixC6,[a] a modifier – Cs-7B,[b] a suppressor – trioctylamine, and a diluent, Isopar® L. This solvent has been used to successfully decontaminate over 2 million gallons of tank waste. However, recent work at Oak Ridge National Laboratory (ORNL), Argonne National Laboratory (ANL), and Savannah River National Laboratory (SRNL) has provided a basis to implement an improved solvent blend. This new solvent blend – referred to as Next Generation Cesium Extraction Solvent (NGCS) – is similar to the current solvent, and also contains four components: the extractant – MAXCalix,[c] a modifier – Cs-7B, a suppressor – a guanidine compound,[d] and a diluent, Isopar® L. Also, the strip acid is changed from dilute (0.001 M) nitric acid to dilute (0.010 M) boric acid. Testing to date has shown that this "Next Generation" solvent promises to provide superior cesium removal efficiencies.

However, performance must be corroborated by compatibility with the current support systems, such as analytical methods.[1] To this end, samples of caustic salt simulant and strip acid were prepared, and spiked with measured quantities of Isopar® ™ L. These samples were then analyzed using the current gas chromatography with flame ionization detector (GC-FID) protocol used at SRNL and F/H laboratories. Samples of dilute boric acid were also prepared to corroborate pH measurements.

2.0 Experimental Procedure

A previously prepared batch of Tank 49H simulant was obtained.[e] A solution of 0.01 M boric acid was also freshly prepared. Both these material were used as the carrier for the traces of Isopar® L added later.

Using these aqueous materials, a set of duplicate samples were prepared. Each sample consisted of 10 mL of either the caustic salt simulant or boric acid and a small mass of hexane-diluted NGCS stock solution.[f] The very small masses made it difficult to accurately weight out the stock solution. The samples were tightly sealed in their glass vial or bottles. Most of the samples (A through L) were prepared in 10 mL p-nut vials with polyethylene caps that were provided to SRNL. The polyethylene lined caps are what F/H lab uses for their sample operations for MCU. Beyond those samples, two additional samples (M and N) were prepared in 15 mL glass vials with Teflon™ caps.

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[a] BOBCalixC6 is short for Calix[4]arene-bis(*tert*-octylbenzo-crown-6)
[b] Cs-7b is short for (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, CAS # 308362-88-1
[c] MAXCalix is short for 1,3-*alt*-25,27-Bis(3,7-dimethyloctyl-1-oxy) calix[4]arene-benzocrown-6
[d] The guanidine compound is N, N'-cyclohexyl, N''-isotridecylguanidine.
[e] This material is identified as "Tank 49H simulant, 5/10/11".
[f] This material is identified as "MAX Solvent Prep #8". For this preparation, the source of the suppressor is LIX-79 ™ from Cognis, for which we are thankful for their generous donation.

Samples were refrigerated until analyzed. Efforts were made to keep the sample upright until used, to avoid contact of the solvent with the lid of the container. These samples were analyzed for Isopar® L content.

For the pH tests, samples of 0.01 M boric acid were used as-is, or serial diluted to 0.001 and 0.0001 M.

One set of samples was sent to F/H laboratory. The other set was sent to AD. In no case were the analysts told of the calculated concentrations of materials.

3.0 Experimental Results

3.1 Isopar® L Analyses

The Isopar® L samples were prepared with the intention of being in the 7-70 mg/L range. Deviation from those goals was caused by the tiny volumes of volatile materials used. In several cases, only a few microliters of stock solution were required. Even utilizing a low-volume electronic pipette, it was impossible to not vary slightly from this intended sample concentration range. Table 1 lists the prepared concentrations and analyzed concentrations for each sample.

Table 1. Calculated and Measured Isopar® L Concentrations in Each Sample

Sample ID	Aqueous Phase	Prepared Concentration (mg/L)	SRNL Analytical Result (mg/L)	F/H Lab Analytical Result (mg/L)	Analyzed÷ Prepared Value "Response"
A	caustic	5.20	<7		
B	caustic	23.6	<7		
C	caustic	47.6	26		0.546
D	caustic	6.10		<5	
E	caustic	26.4		5.65	0.213
F	caustic	46.9		29.5	0.629
M	caustic	32.8	34.0		1.04
G	boric acid	17.0	<7		
H	boric acid	39.0	22		0.563
I	boric acid	62.0	49		0.790
J	boric acid	20.5		8.02	0.391
K	boric acid	42.8		31.8	0.742
L	boric acid	61.9		53.7	0.868
N	boric acid	56.5		55.4	0.980

The analytical uncertainty for SRNL and F/H Lab is 20% for each sample.

With the limited number of data points, it is difficult to discern clear or distinct trends. Prior studies have a far larger data set than this one.[2] Nevertheless, the general trend in agreement is similar to the prior study. Below, we discuss several trends.

- At very low levels (<10 mg/L), both labs report detection limits. While the F/H Lab detection limit is slightly lower than for SRNL (i.e., <5 *vs.* <7 mg/L, respectively), samples prepared at <10 mg/L are all analyzed at less-than values. Not until prepared samples are in the 20 mg/L or higher range do we get a measured (not less-than) value.

- The lower the Isopar® L concentration in the sample, the greater the offset between the prepared and analyzed values. A simple way to examine this is to divide the analyzed result by the prepared result (see the right-most column in Table 1) to derive a “response”. As the prepared sample concentrations decline, so does the response.

- The aqueous phase (caustic salt simulant *vs.* boric acid solution) does not appear to have an effect on the results.

- All of the sample results are biased low, with the exception of sample M, which was very slightly above the prepared value. This would suggest that we are losing Isopar® L from the samples, even though we took efforts to prevent loss.

- The response of SRNL analyses compared to F/H Lab analyses is similar. It does not appear that SRNL or F/H Lab results are markedly different.

- Samples M and N appear to have more reliable analyses given their prepared values. These two samples were prepared in 15 mL glass vials with Teflon™ caps, and SRNL attributes this better response to this different storage media. The Teflon™ caps should sorb and hold less Isopar® L from the sample, which means less negative bias in the sample results.

3.1 pH Analyses

For the pH standards, the researchers started by preparing a bottle of 0.01 M boric acid (measured 0.0628 grams of boric acid diluted to 100 mL with deionized water). Volumes of this material were then serially diluted with an electronic pipette to generate the 0.001 and 0.0001 M boric acid solutions. See Table 2.

SRNL used an Accumet Basic AB 15 pH probe after a two point calibration. F/H lab used a Thermo Orion A+ series pH meter after a two point calibration.

Table 2. Calculated pH Values in Each Sample

Sample ID	Calculated pH	SRNL Analytical Result (pH)	F/H Lab Analytical Result (pH)
P	5.63	6.96	
Q	5.63		6.62
R	6.13	7.31	
S	6.13		7.01
T	6.63	7.73	
U	6.63		6.92

The calculated value is from knowing the dissociation constant, K_a to be 5.31E-10 (at 20.6 °C).[3]

While previous work examined a pH crosscheck between SRNL and F/H Lab, this was for more concentrated strong acids, which are easier to measure.[4]

The offset between the calculated values and the measured values is surprisingly great. Both SRNL and F/H Lab took pains to calibrate the pH meters, and both gave roughly similar results. The majority of the results are an integer pH unit (biased high) from the calculated values, which is an order of magnitude off.

As a confirmation, SRNL analyzed its three solutions using two different types of pH paper. In both cases, the pH paper was further off from the calculated result than the pH meters were, in the opposite bias.

The results indicate that it is inherently difficult to measure the pH of solutions of very dilute boric acid, either by pH paper or meter. Boric acid is a weak acid and dilute in this application, resulting in a solution that is very easily disturbed, even by atmospheric carbon dioxide uptake. SRNL would propose that instead of measuring the pH of boric acid solutions, the program considers measuring the boron content by Inductively Coupled Plasma Emission Spectroscopy (ICPES), which has a far superior sensitivity. Alternatively, SRNL will examine whether or not titration methods would provide better results.

4.0 Conclusions

In this latest round of crosschecks, the limited dataset indicate limited offset between SRNL and F/H Lab measurements for Isopar® ™ L analysis at higher concentrations. However, there is a clear low bias for samples that were prepared at ~20-50 mg/L of Isopar® ™ L, common to both SRNL and F/H Lab. SRNL recommends re-examining whether it is possible to use Teflon™ lined caps for use during sample collection and analysis to mitigate analyte uptake by the container lid.

With regards to pH measurements, dilute solutions of boric acid are clearly difficult to cleanly measure. SRNL would recommend using ICPES boron analysis as a substitute, given the far greater sensitivity of that analytical method.

Appendix I

Control Data for the SRNL for Isopar ® L and pH Analyses

Isopar ® L Analyses: Each sample was prepared as outlined in AD Procedure 2657, recorded in notebook SRNL-NB-2010-00128, & analyzed by GC-FID.

Gas Chromatography with Flame Ionization Detector (GC - FID) analysis was employed to identify organic compounds in the samples. Analyses were carried out in building 773-A, laboratory B-123. It should be noted that AD is not certified by DHEC for NPDES discharge compliance monitoring.

Analytical separations were carried out on a Hewlett Packard 6890 gas chromatograph, equipped with a 25 m DB-5 column, with 0.20 mm diameter and 0.33 um film thickness. Quantitation was performed using a flame ionization detector.

As part of a quality control effort, a matrix spike recover sample was analyzed in duplicate. The first matrix spike recovery was 116%, based on a 40 mg/L LCS. The second matrix spike duplicate recovery was 119%, based on a 40 mg/L LCS.

pH Analyses: The pH probe was confirmed with known pH standard solutions. A pH 7 standard measured 7.05, and a pH 10 standard measured 9.96.

Control Data for the SRNL for Isopar ® L and pH Analyses

Isopar ® L Analyses: Each caustic sample matrix was prepared and analyzed by GC-FID as outlined in L3.05-10126. Each acidic sample matrix was prepared as outlined in L3.06-10133 and analyzed by GC-FID as outlined in L3.05-10126.

A Thermo Trace 200 Gas Chromatography with Flame Ionization Detector (GC - FID) analysis was employed to identify organic compounds in the samples. Analyses were carried out in building 772-F, laboratory 131. The GC-FID is equipped with a 30 m DB-1 column, with 0.53 mm diameter and 1 um film thickness.

As part of a quality control effort, the Quality Control (QC) standard that is routinely analyzed along with caustic or acidic samples was analyzed along with the corresponding sample matrix. The caustic QC result was 7.33 mg/L, based on a 7.0 mg/L known concentration. The acidic QC result was 36.23 mg/L, based on a 40.0 mg/L known concentration.

pH Analyses: The acidic sample matrix was analyzed for pH using L3.06-10132. The pH probe was calibrated using pH 4 and pH 7 buffer solutions. As part of a quality control effort, the Quality Control (QC) standard that is routinely analyzed along with the acidic samples was analyzed along with the samples. The pH QC result was 2.99, based on a known pH of 3.00.

5.0 References

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